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Dedicated to Professor Henryk Koroniak (Poznań) on the occassion of his 70th birthday

Abstract: The mechanism of the reaction of diphenyldiazomethane with thiobenzophenone and related hetaryl thioketones leading to the corresponding tetrasubstituted thiiranes was studied by means of DFT computational methods at the M06-2X/6-311+G(d) level of theory. The study showed that the initial step of this conversion is a classic one-step (3+2) cycloaddition to give 1,3,4-thiadiazolines in a regioselective manner. These initially formed products undergo a spontaneous extrusion of N_2 resulting in the formation of tetraaryl substituted thiocarbonyl ylides as reactive intermediates. The calculated parameters of the activation for the subsequent 1,3-dipolar electrocyclizations are low (ΔG = 10.8 – 11.9 kcal/mol) and the only products formed in these reactions are the corresponding thiiranes. The alternative pathways leading to thiocarbonyl ylides via stepwise mechanisms involving zwitterionic or biradical nitrogen-containing intermediates were ruled out.

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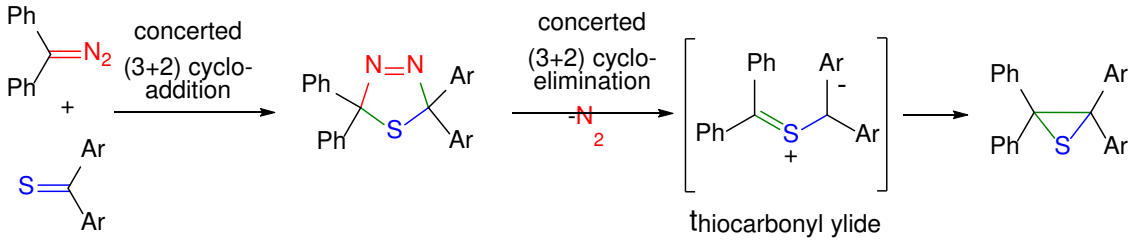
Keywords: Reaction mechanisms, Diaryldiazomethanes, Thioketones, Thiiranes, Computational study, Molecular Electron Density Theory

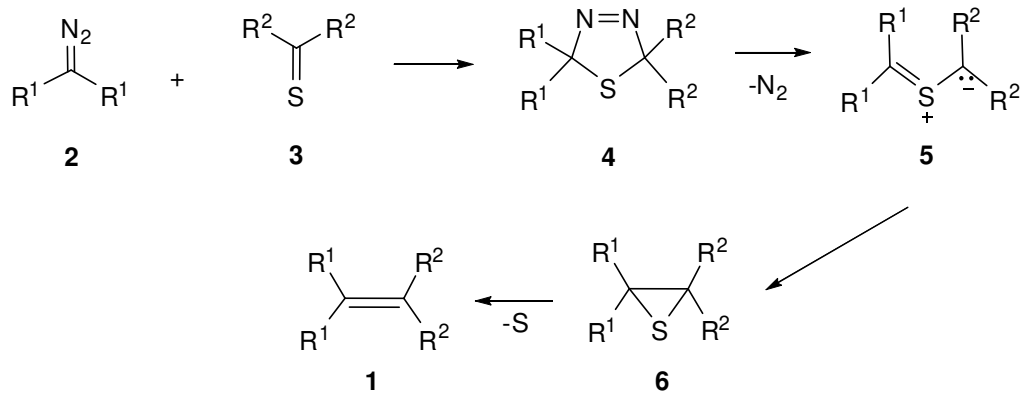
Graphical abstract:



Graphical abstract-text: The mechanism of the reaction of diphenyldiazomethane with thiobenzophenone and related thioketones, leading to the corresponding tetrasubstituted thiiranes was studied by means of DFT computational methods at the M06-2X/6-311+G(d) level of theory. The study demonstrated that the initial step of this multi-step conversion is a classic one-step (3+2) cycloaddition leading to an unstable 1,3,4-thiadiazoline in a regioselective manner.

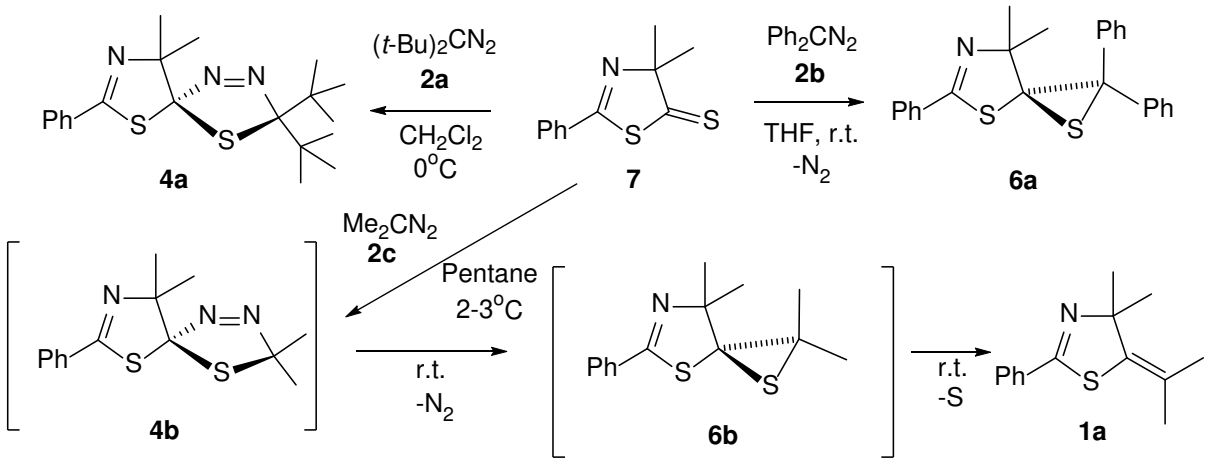
Introduction

The Barton-Kellogg reaction comprises the synthesis of substituted ethylenes **1** via the so-called two-fold extrusion reaction starting with a diazomethane **2** as three atom component (TAC) and a thiocarbonyl compound **3**.[1] The mechanistic explanation of the reaction course is based on the assumption that the initially formed 1,3,4-thiadiazoline **4** extrudes N_2 to generate the corresponding unstable thiocarbonyl ylide **5** (Scheme 1). The latter intermediate undergoes a conrotatory ring closure yielding a thiirane derivative **6**. Depending on its stability, the sulfur atom is extruded spontaneously or has to be removed by treatment with a phosphine to give ethylene **1**. Along with other well-established protocols, the Barton-Kellogg reaction offers a convenient and widely applied access to C=C-containing compounds (olefination reactions) with special importance for the preparation of sterically crowded olefins.[2]



Scheme 1. The course of the Barton-Kellogg reaction.

In spite of the fact that the first reactions of thiocarbonyl compounds with diazomethanes **2** were published in the 1920ties,[3] the elucidation of the reaction mechanism was reported by Huisgen only 60 years later.[4] Depending on the type of thiocarbonyl compound **3** and diazomethane derivative **2**, different final products can be obtained in these reactions. For example, reactions performed in our laboratories with 1,3-thiazole-5(4*H*)-thione **7** and differently substituted diazomethanes **2** led to a variety of products shown in Scheme 2. For example, in the reaction of **7** with bis(*tert*-butyl)diazomethane (**2a**), the initial (3+2) cycloadduct, i.e. 1,3,4-thiadiazoline **4a**, was isolated and identified.[5a] In contrast, the reaction with diphenyldiazomethane (**2b**) occurred at room temperature with evolution of N_2, and thiirane **6a** was obtained as the product of the electrocyclization of the intermediate thiocarbonyl ylide.[5a] Finally, in the case of 2-diazopropane (**2c**), an unstable 1,3,4-thiadiazoline **4b** was observed by ^{1}H NMR spectroscopy, but spontaneous elimination of N_2 resulted in the formation of thiirane **6b**, which extruded spontaneously sulfur to give the respective ethylene derivative **1a**.[5b] A more complex reaction was observed using diazomethane at low temperature, and a mixture of products resulting from competitive reactions of the intermediate thiocarbonyl ylide of type **5**, i.e. electrocyclization ($\rightarrow$ thiirane), (3+2) cycloaddition with the starting **7** ($\rightarrow$ 1,3-dithiolane), as well as head-to-head dimerization ($\rightarrow$ 1,4-dithiane), was obtained in these cases.[5c]



Scheme 2. Presentation of (3+2) cycloaddition reactions of differently substituted diazomethanes **2** with 1,3-thiazole-5(4*H*)-thione **7**.

The reaction of diaryldiazomethane derivatives such as diphenyldiazomethane (**2b**) or 9-diazofluorene (**2d**) with aryl, hetaryl, and ferrocenylthioketones of type **3** have been widely studied and offer a straightforward access to tetrasubstituted ethylenes[6] and dibenzofulvenes.[7] This general concept based on reactions of diaryldiazomethanes with diaryl and ferrocenylthioketones was successfully applied for the preparation of precursors of molecular machines[8] and some drugs, e.g. ferrocifens,[9] respectively. Notably, reactions of that type occurred at room temperature and in none of the described experiments the formation of the anticipated initial (3+2) cycloadduct was observed. Instead, secondary products such as thiiranes or corresponding ethylenes formed therefrom were obtained. For that reason, the important question should be answered whether the first step of the reaction of diarylthioketones **3** (R^2 = Ar) with diaryldiazomethanes **2** (R^1 = Ar) occurs via a one-step (3+2) cycloaddition followed by cycloelimination of N_2 or N_2 is extruded from a zwitterionic/biradical intermediate. Notably, in none of the reactions of that type, the formation of tetraaryl substituted 1,3-dithiolanes as products of the trapping reaction ((3+2) cycloadditions) of the intermediate thiocarbonyl ylides **5** with the starting thioketone **3** was observed.[6]

The discussion on the mechanism of cycloaddition reactions is an important issue in the development of the theory of organic reaction mechanisms. On the basis of the old, traditional view on the mechanism of (3+2) cycloaddition reactions,[10,11] the analyzed processes should proceed according to a one-step, "pericyclic" mechanism. However, in recent time, Domingo[12] generally undermined the term "pericyclic" regarding most examples

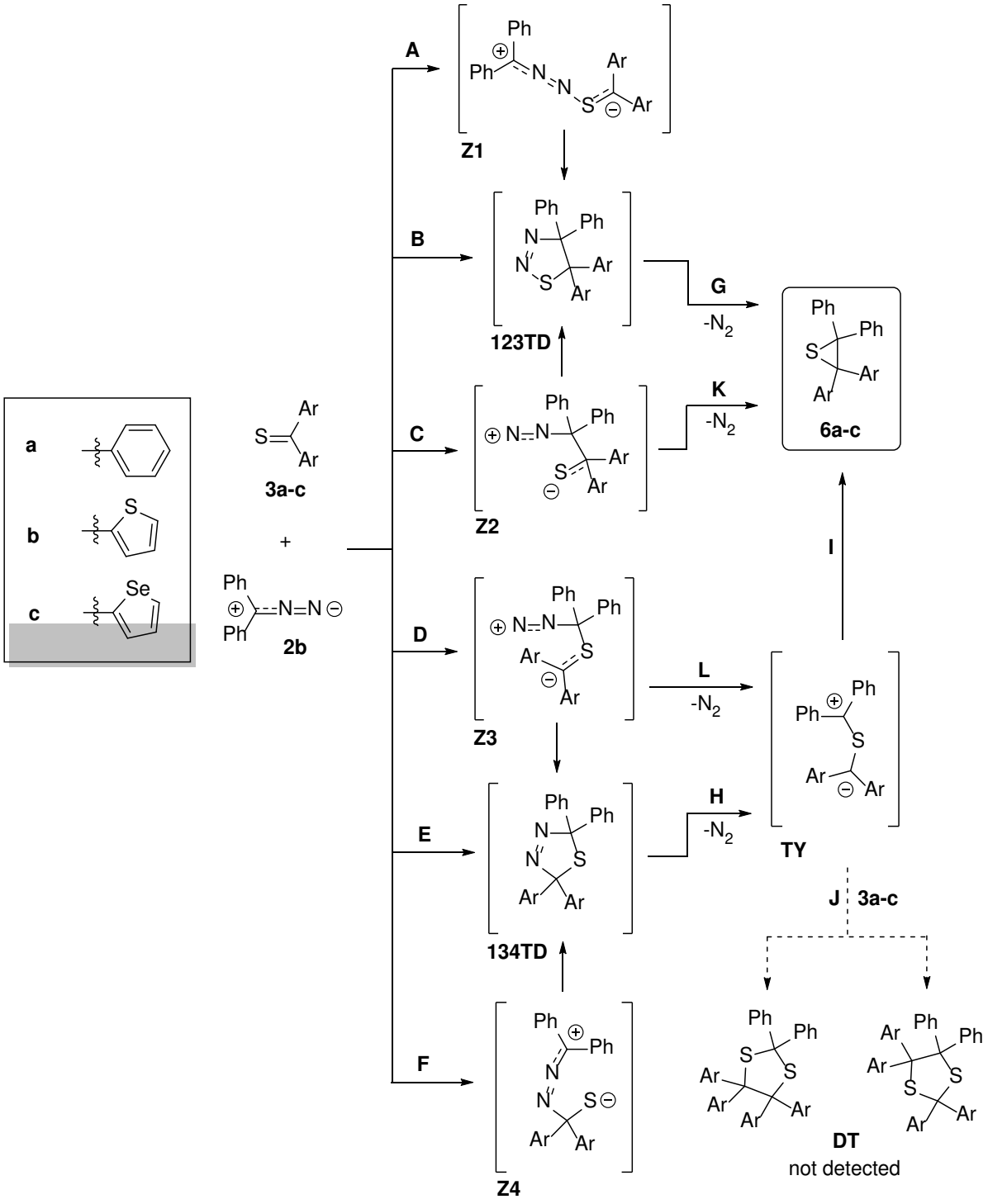
of cycloadditions. This point of view was confirmed very recently also by other theoretician chemists.[13–17] In addition, some examples of reactions involving diaryl diazomethanes and different types of ethylene derivatives have been explored recently using comprehensive experimental and quantum chemical methods.[18,19] It has been found that the initial stage of these reactions is the formation of a zwitterionic intermediate.

On the other hand, hetarylthioketones were also shown to react stepwise with some TACs. For example, their reactions with in situ generated thiocarbonyl *S*-methanides afforded 1,3-dithiolanes and isomeric 14-membered heterocyclic systems.[20] The formation of the latter was explained via a stepwise mechanism with the intermediacy of a delocalized diradical species, and this interpretation was supported by an independent computational study.[21] The (3+2) cycloaddition reactions with alkyl and trimethylsilyl-substituted diazomethanes with hetaryl thioketones were also postulated to follow a stepwise mechanism.[22]

The goal of the present study was the elucidation of the reaction mechanism of the model (3+2) cycloadditions of selected diaryl thioketones **3a**–**c** with diphenyldiazomethane (**2b**) by means of computational methods.

Results and Discussion

Reactions of diaryldiazomethanes **2** (R^1 = Ar) with aryl, hetaryl, and ferrocenyl thioketones **3** (R^2 = Ar, Hetar, Ferrocenyl) are well known and, depending on the substitution pattern, lead to thiiranes or tetrasubstituted ethylenes.[3,23,24] Several different reaction pathways leading to the postulated 1,3,4-thiadiazolines as initially formed products can be considered (Scheme 3). In particular, in addition to the one-step mechanism mentioned above (paths **B**,**E**), stepwise, zwitterionic mechanisms (paths **A**,**C**,**D**,**F**) should not be a priori excluded. The zwitterionic mechanism is in the analyzed cases evidently supported by the unequivocal degree of the screening of the reaction centers of both addends. In particular, one of the reaction centers is always strongly shielded by bulky substituents, whereas the second reaction site is fully unprotected. In summary, all considered reaction mechanisms are presented in Scheme 3.



Scheme 3. Studied reaction paths for the formation of thiiranes **6a**–**c** in multi-step reactions of diphenyldiazomethane (**2b**) with aryl/hetaryl thioketones **3a**–**c**.

Firstly, we decided to shed some light on the nature of the intermolecular interactions in the initial stage of the model reactions. Recently, we analyzed the global and local

properties of diphenyldiazomethane **2b**.[18] The study showed that this molecule exhibits evidently nucleophilic character (global nucleophilicity N = 3.91 eV), with concentration of the most local nucleophilic power[25] on the terminal nitrogen atom of the >CNN moiety (N_N = 1.62 eV).

On the other side, the three considered thioketones are characterized by evidently electrophilic properties (Table 1). In particular, the global electrophilicity power for thiobenzophenone (**3a**) is equal 2.61 eV. This value is identical with that in the case of nitroethene,[16] which is known as a very reactive component in many cycloaddition processes.[16,26,27] According to Domingo's reactivity scale,[28,29] this compound should be classified as a strong electrophile. The replacement of the phenyl rings by five-membered hetaryl rings leads to enhancement of the electrophilic power of the thioketone molecule. This effect is stronger to some degree when the heteroatom is characterized by a lower value of the electronegativity. For example, the global electrophilicity of the di(thiophen-2-yl) thioketone (**3b**) is equal 2.94 eV, whereas the analogous parameter for the di(selenophen-2-yl) thioketone (**3c**) is higher than 3eV.

The distribution of the electrophilicity power on the potential reaction sites of thioketones is not uniform within the whole molecule. In particular, the most electrophilic atom within the >C=S group is always the carbon atom (local electrophilicity in the range of 0.98–1.00 eV). Thus, the nature of local nucleophile-electrophile interaction favors in all considered cases the formation of the hypothetical 1,3,4-thiadiazoline **134TD** via a single-step cycloaddition (path **E**) or a stepwise mechanism with a zwitterionic intermediate (path **D** or **F**). The theoretically possible pathways **A**–**C** are disfavored in the light of the Molecular Electron Density Theory (MEDT).[30]

Table 1. Global and local electronic properties of diphenyldiazomethane (**2b**) and thioketones **3a**–**c**.

Comp.	Global properties				Local properties							
	μ [eV]	η [eV]	ω [eV]	N [eV]	P^+_C	P^+_S	ω_C [eV]	ω_S [eV]	P^-_C	P^-_N	N_C [eV]	N_N [eV]
2b	–3.36	3.70	1.52	3.91					0.23	0.41	0.91	1.62
3a	–4.10	3.23	2.61	3.40	0.38	0.33	1.00	0.85				
3b	–4.25	3.08	2.94	3.33	0.33	0.28	0.98	0.84				
3c	–4.27	3.01	3.03	3.34	0.33	0.27	0.99	0.82				

The analysis of local interactions suggests that the formation of regioisomeric 1,2,3-thiadiazoline intermediates is possible, but it does not indicate the molecular mechanism of their formation. For this purpose, deeper exploration of theoretically possible reaction paths with localization and identification of all critical structures is necessary. This study was initiated by analysis of the (3+2) cycloaddition of diphenyldiazomethane (**2b**) with thiobenzophenone (**3a**) (Tables S1 and S2 in the SI part). The nature of the energy profiles for competitive reactions leading to the regioisomeric thiadiazolines **123TD** and **134TD** are presented in Figure 1. The results of the M06-2X/6-311+G(d) computational study show that, in both cases, the conversion of addends into (3+2) cycloadducts proceed via single transition states TSs (**TSB** and **TSE**, respectively). All attempts to optimize structures, which could be considered as potential zwitterionic intermediates, were unsuccessful. So, the stepwise mechanism of the formation of the thiadiazoline ring in the analyzed reaction should be excluded.

The nature of reaction profiles for competitive channels **B** and **E** is similar (Figure 1), but their quantitative description is substantially different (Table 2). In particular, the Gibbs free energy of activation for path **B** is equal 25.6 kcal/mol, whereas it is lower than 20 kcal/mol for the competitive path **E**. Thus, from the kinetic point of view, the reaction channels leading to the 1,2,3-thiadiazoline (**123TD**) should be regarded as hindered processes. It should be underlined that low enthalpy of activation (Table 2), allows the reaction to occur at low temperature, what is in full agreement with the experimental observations.[6] The geometries of the TSs of the competitive reaction paths are rather similar (Figure 2, Tables S3, S5, S13 and S14 in the SI part). In particular, within these TSs, two new single bonds, namely C3–C4 and S5–N1 bonds (in the case of **TSB**) or C3–S4 and C5–N1 bonds (in the case of **TSE**), are always formed. In all cases, some differences of synchronicity of new bonds development are observed (Tables S13 and S14 in the SI part). This non-synchronicity is however not sufficient to enforce the stepwise mechanism of the formation of the target heterocyclic ring. It is interesting that the electronic nature of **TSB** and **TSE** is substantially different. In the light of MEDT,[30] the first analysed **TSB** should be considered as a structure which is typical for non-polar (3+2) cycloadditions, whereas **TSE** exhibits an evidently polar nature. This is confirmed by analysis of the Global Electron Density Transfer (GEDT) values (Tables S13 and S14 in the SI part). So, our observations regarding the polarity and energetic aspects of the discussed TSs are fully compatible with the postulate of polar acceleration in cycloaddition processes.[31]

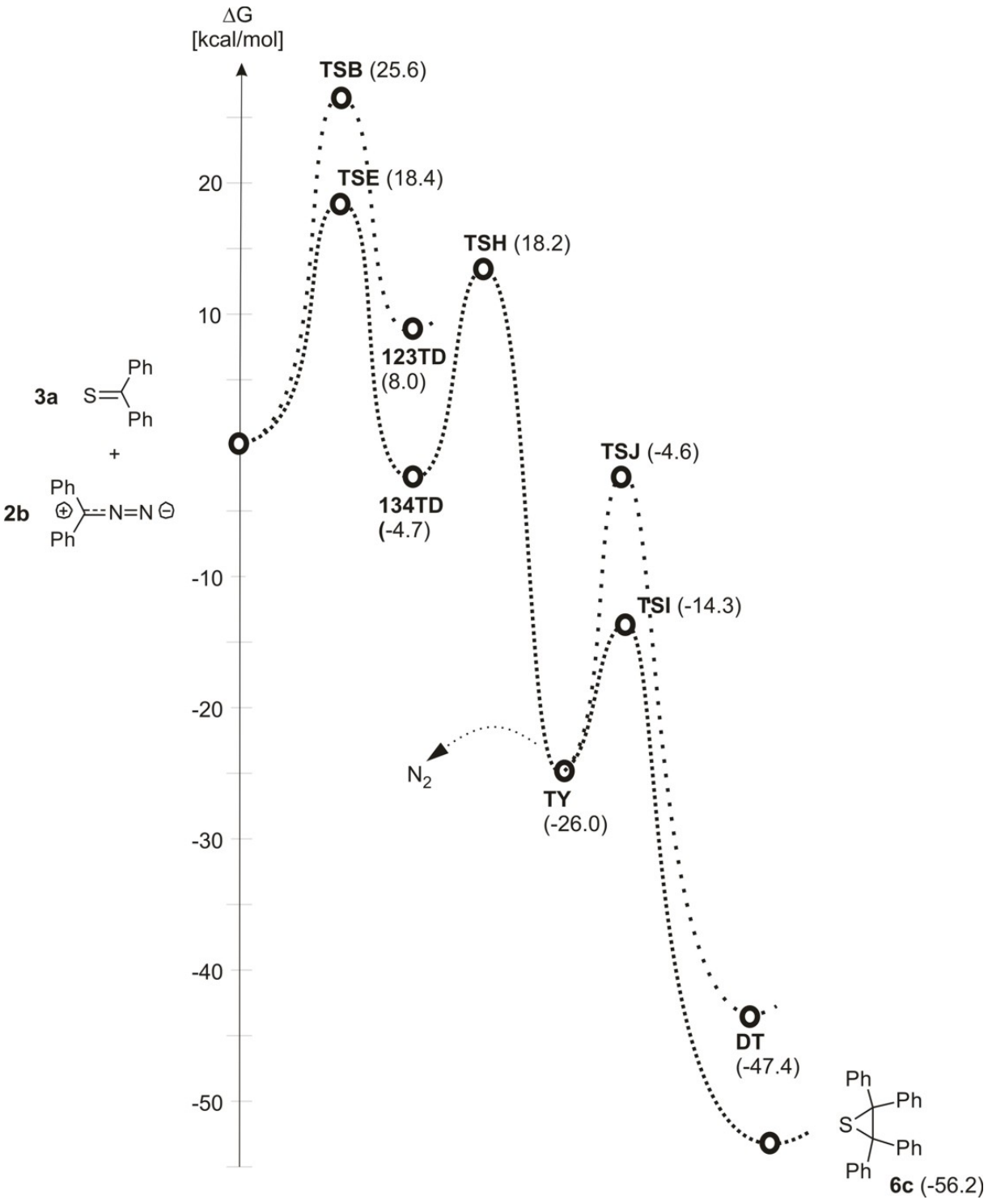
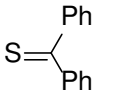
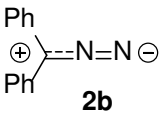
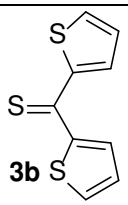
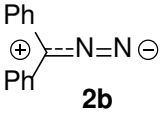
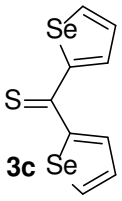
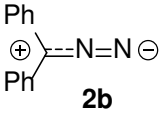


Figure 1. Gibbs free energy profiles for the reaction between diphenyldiazomethane (**2b**) and thiobenzophenone (**3a**) in Et_2O solution, according to the M06-2X/6-311+G(d) (PCM) computational study. The corresponding free energies to each point with respect to reagents (**2b**+**3a**) are presented in brackets.

Table 2. Kinetic and thermodynamic parameters of the reaction between diphenyldiazomethane (**2b**) and thioketones **3a–c** in Et_2O solution, according to the M06-2X/6-311+G(d) (PCM) computational study (ΔH, ΔG values are expressed in kcal/mol; ΔS values are expressed in cal/molK).

Reaction	Path	Transition	ΔH	ΔG	ΔS
 **3a** +  **2b**	**B**	**2b + 3a → TSB**	8.2	25.6	–58.3
		2b + 3a → 123TD	–8.9	8.0	–56.5
	E	**2b + 3a → TSE**	4.5	18.4	–46.6
		2b + 3a → 134TD	–20.2	–4.7	–52.0
	H	**134TD → TSH**	18.3	18.2	0.5
		134TD → TY	–9.9	–21.3	38.3
	I	**TY → TSI**	9.0	11.7	–9.2
		TY → 6c	–29.8	–30.1	1.2
	J	**TY + 3a → TSJ**	5.9	21.4	–51.9
		TY + 3a → DT	–38.1	–21.0	–57.1
 **3b** +  **2b**	**B**	**2b + 3b → TSB**	8.1	25.4	–58.0
		2b + 3b → 123TD	–6.4	10.0	–54.9
	E	**2b + 3b → TSE**	6.2	20.7	–48.5
		2b + 3b → 134TD	–17.2	–2.1	–50.8
	H	**134TD → TSH**	18.3	18.5	–0.5
		134TD → TY	–9.9	–21.7	39.4
	I	**TY → TSI**	10.5	11.9	–4.9
		TY → 6d	–29.5	–28.1	–2.3
 **3c** +  **2b**	**B**	**2b + 3c → TSB**	8.8	26.4	–59.2
		2b + 3c → 123TD	–4.8	11.4	–54.3
	E	**2b + 3c → TSE**	6.3	20.6	–47.8
		2b + 3c → 134TD	–14.7	–1.0	–46.0
	H	**134TD → TSH**	16.2	18.2	–6.5
		134TD → TY	–12.1	–22.2	33.8
	I	**TY → TSI**	9.5	10.8	–4.2
		TY → 6e	–29.2	–28.6	–2.0

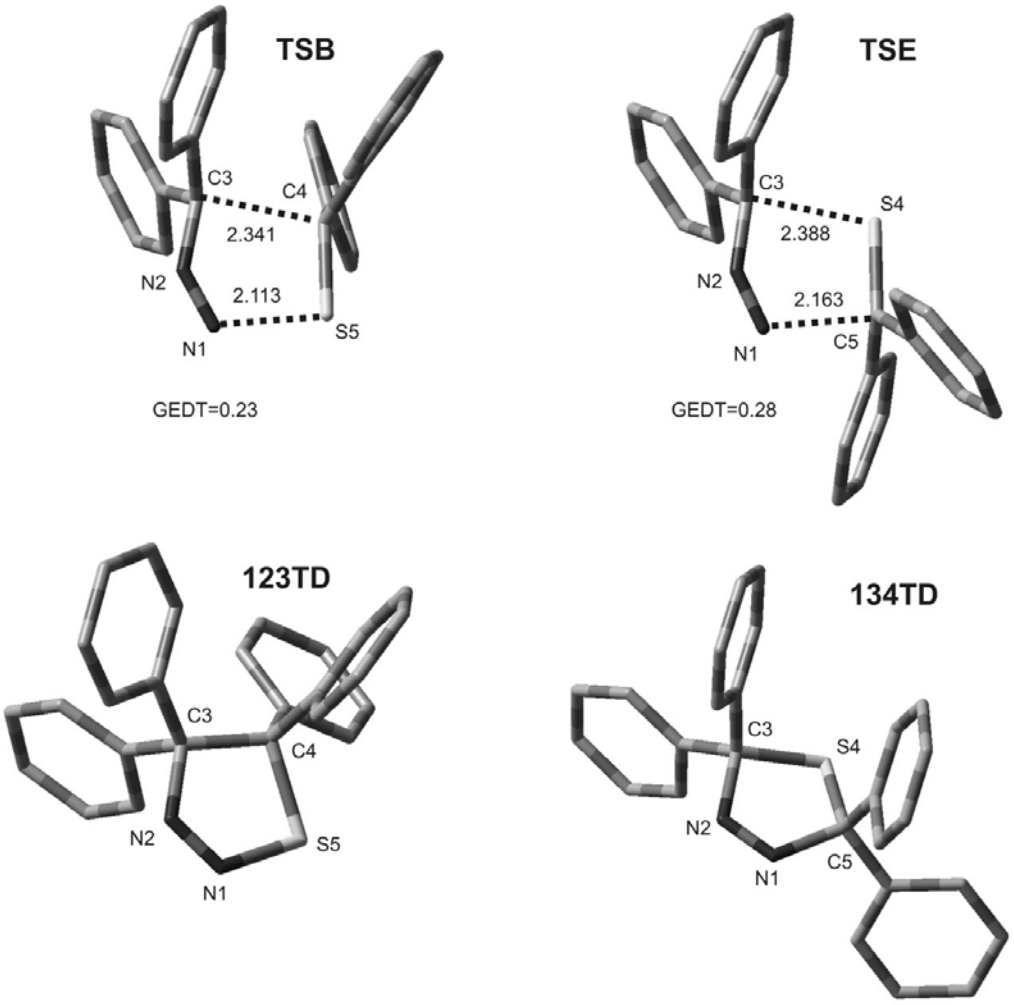


Figure 2. Views of key structures for paths **B** and **E** of the reaction between diphenyldiazomethane (**2b**) and thiobenzophenone (**3a**) in Et_2O solution, according to the M06-2X/6-311+G(d) (PCM) computational study. Key interatomic distances are given in [Å]; GEDT values are given in [e].

The further transformation of **TSB** and **TSE** leads directly to the respective (3+2) cycloadducts. It should be underlined that the formation of the hypothetical **123TD** molecule is not favored also from the thermodynamic point of view, because its Gibbs free energy of formation is equal 8.0 kcal/mol. This value suggests clearly that the equilibrium of the formation of **123TD** is fully shifted into the substrate area. At the same time, the Gibbs free energy of the process leading to **134TD** is equal –4.7 kcal/mol. This allows the formation of **134TD** as a more stable intermediate.

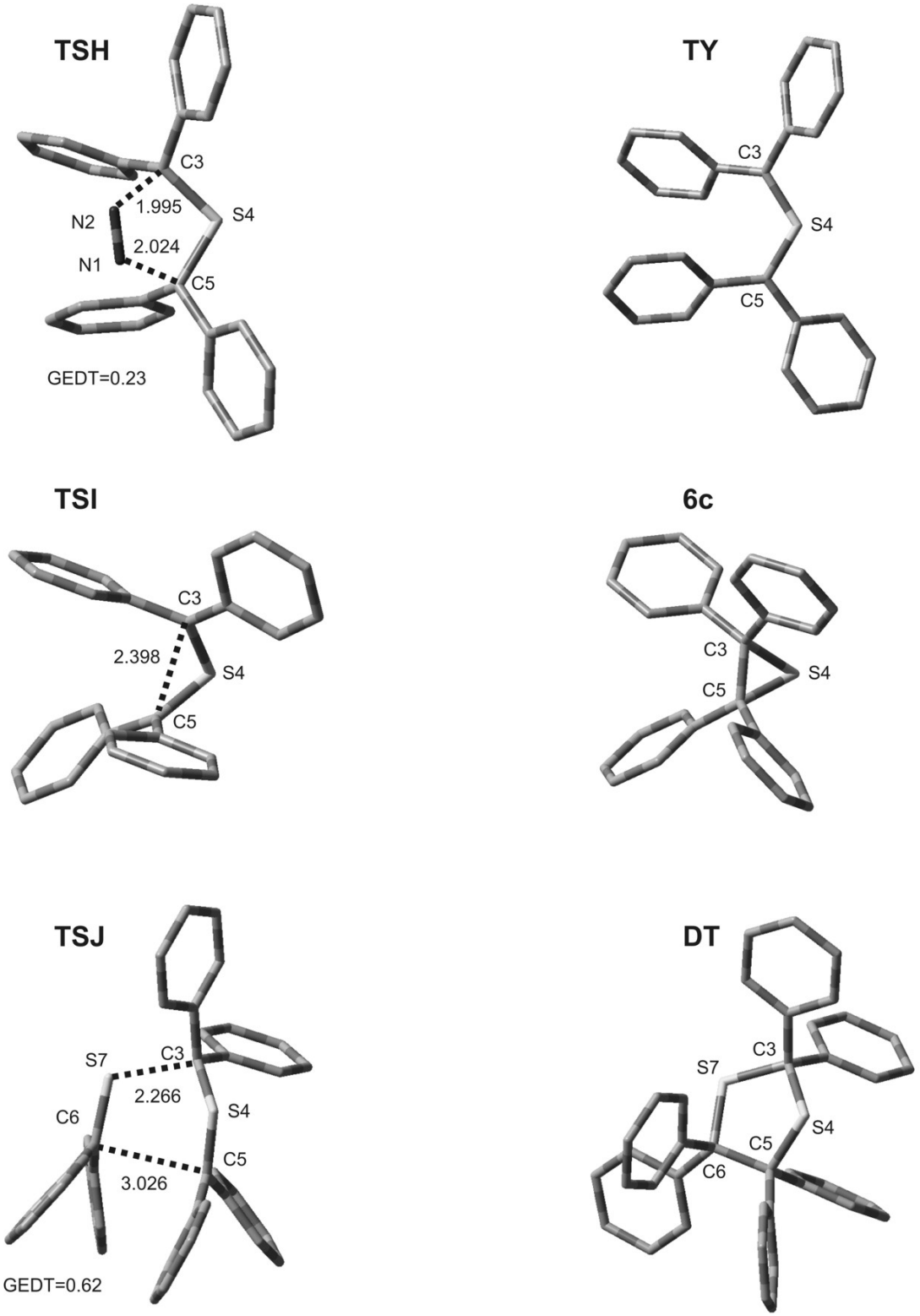


Figure 3. Views of key structures for paths **I**, **H**, **J** of the reaction between diphenyldiazomethane (**2b**) and thiobenzophenone (**3a**) in Et_2O solution, according to the M06-2X/6-311+G(d) (PCM) computational study. Key interatomic distances are given in [Å]; GEDT value is given in [e].

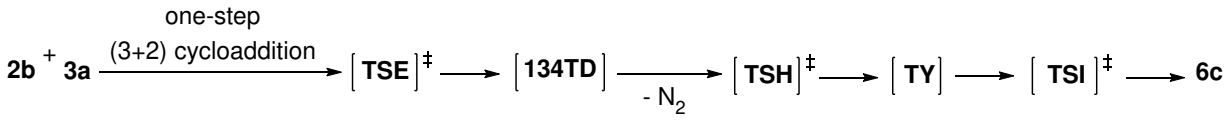
The subsequent reaction of 1,3,4-thiadiazoline **134TD** proceeds via N_2-elimination. This process is realized via the transition state **TSH** (Figures 1 and 3, Table 1) and requires overcoming the activation barrier of ΔH = 18.2 kcal/mol, which is very similar as in the case of the (3+2) cycloaddition reaction (**2b** + **3a** → **134TD**, Table 2). In addition, the thermodynamic factors are totally conducive for shifting the reaction equilibrium into the area of the product (ΔG of the reaction is equal –21.3 kcal/mol). This value explains without any doubts why the **134TD**s are not detected experimentally as intermediates in the studied (3+2) cycloaddition reaction. Within the **TSH**, two C–N bonds are ruptured (Tables S7 and S15 in the SI part). This process is characterized by high synchronicity of the dissociation of the two C–N bonds. Additionally, **TSH** exhibits moderate polar nature, which is confirmed by the GEDT value (0.23 e). Similar transition states have been described in our earlier study for thermal decomposition of pyrazoline systems derived from diaryldiazomethanes and dimethyl (*E*)- and (*Z*)-2,3-dicyanobutenedioates.[18] The intrinsic reaction coordinate (IRC) calculations performed for the **TSH** linked this structure with the values which can be connected with the starting molecule as well as with the mixture of the **TY** intermediate and the N_2 molecule. The **TY** molecule exhibits the nature of a thiocarbonyl ylide and can be converted via a single-step cyclization into the tetraphenylthiirane (**6a**). The results of the M06-2X/6-311+G(d) computational study show (Table 2 as well as Tables S9, S10 and S15 in the SI part) that this process is realized via a single transition state (**TSI**) (Table S9 in the SI part). This requires a relatively low Gibbs free energy of activation (11.7 kcal/mol). From the thermodynamic point of view, this transformation is completely irreversible (ΔG = –30.1 kcal/mol).

Theoretically, the **TY** intermediate (thiocarbonyl ylide) can be further converted into a respective 1,3-dithiolane via (3+2) cycloaddition involving a second thioketone molecule as a dipolarophile (path **J**). The cycloaddition process **TY**+**3a** is connected with a barrier of activation (**TSJ** – see Figure 3 as well as Tables S11 and S16 in the SI), which is higher than 20 kcal/mol, and, therefore, should be considered as a hindered process from the kinetic point of view.

At this point, one should mention that the key steps of the considered reaction were re-examined on the basis of the quantum-chemical calculations using larger basis sets. It was found that geometrical parameters of obtained structures are practically identical as in the case of calculations performed at the M06-2X/6311+G(d) level of theory. Furthermore, activation parameters calculated using different basis sets differ slightly, only. In all cases, the quantum-

chemical calculations suggest identical kinetic and thermodynamic preferences for the analyzed reaction paths (see Table S17 in the SI).

Thus, the molecular mechanism of the reaction between diphenyldiazomethane (**2b**) and thiobenzphenone (**3a**) should be considered as a three-step reaction, which is initiated by the (3+2) cycloaddition process leading to 2,2,5,5-tetraphenyl-1,3,4-thiadiazoline **134TD**. All alternative channels for the reaction system (Scheme 3) are hindered from the kinetic and (in some cases) from the thermodynamic point of view. The general scheme of this transformation is depicted in Scheme 4.



Scheme 4. Reaction sequence of the formation of thiirane **6c** from diphenyldiazomethane (**2b**) and thiobenzophenone (**3a**) (see also Scheme 3 as well as Figures 1–3).

On a similar way, we analyzed analogous reactions involving di(hetaryl) thioketones **3b**–**c**. It was found that the kinetic preference of possible reaction paths is identical as in the case of the reaction **2b**+**3a** (see Table 2 and Tables 13–16 in the SI part). Next, the molecular mechanism of the conversion of the addends into the respective thiirane systems is also analogous. So, the proposed Scheme 4 can be considered as general mechanism for a larger group of reactions between sterically crowded diazocompounds and diarylthioketones.

Conclusions

The (3+2) cycloadditions of aromatic thioketones with differently substituted diazomethanes are known to occur at low temperature (< –40 °C). Whereas reactions with the parent diazomethane or (trimethylsilyl)diazomethane afford under these conditions stable 1,3,4-thiadiazoline derivatives, the analogous reactions with diaryldiazomethanes result in the immediate evolution of N_2. The present study demonstrated that N_2 is eliminated from the initially formed unstable (3+2) cycloadducts and not from zwitterionic intermediates. The tetraryl substituted thiocarbonyl ylides formed thereby undergo preferred electrocyclization reactions leading to three-membered thiiranes. Due to the higher activation enthalpies, the alternative (3+2) cycloaddition with another thioketone molecule, leading to a 1,3-dithiolane derivative, does not take place. Very likely, similar factors and steric hindrance prevent the

dimerization of tetraaryl substituted thiocarbonyl ylides. For all these reasons, reactions of diphenyldiazomethane with aryl and hetaryl-substituted thioketones lead to tetrasubstituted thiiranes as exclusive products, which are key intermediates to prepare desired tetraryl substituted ethylenes as the final products of the Barton-Kellogg reaction.

Experimental Section

All quantum-chemical calculations were performed using 'Prometheus' cluster (CYFRONET regional computational centre). The M06-2X functional[32] included in the GAUSSIAN 09 package[33] and the 6-311+G(d) basis set including both diffuse and polarization functions for all relevant atoms was used. For the model transformations, other, larger basis sets (6-311+G(d,p) and 6-311++G(d)), have been also included to perform the calculations (see SI). All localised stationary points have been characterized using vibrational analysis. It was found that starting molecules as well as products had positive Hessian matrices. On the other hand, all transition states (**TS**) showed only one negative eigenvalue in their Hessian matrices. For all optimized transition states, intrinsic reaction coordinate (IRC) calculations have been performed. The hypothetical, biradical nature of intermediates has carefully been verified using UM06-2X/6-311+G(d) computational study, analogously as in our previous work.[34] The presence of the solvent in the reaction environment (diethyl ether, ε = 4.24) has been included using IEFPCM algorithm.[35] Global electron density transfer between substructures of the TS (GEDT)[36] was calculated according to the equation:

$$GEDT=\Sigma q_A$$

where q_A is the net charge, and the sum is taken over all the atoms of the thioketone.

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